III.B Fuel Processing

III.B.1 Technology Development in Support of the Solid State Energy Conversion Alliance

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Objectives

- Improve the thermal stability of reforming catalyst for diesel fuel.
- Improve the sulfur tolerance of the catalysts.
- Characterize the catalytic activity.
- Determine long-term stability.

Approach

- Synthesize and characterize perovskites that are stable in hydrogen and oxygen and have redox chemistry on the "B" site.
- Explore the effects of different dopants on the A and B sites.
- Verify that the doped catalysts are chemically and thermally stable and relatively unaffected by sulfur-containing fuel.

Accomplishments

- A class of perovskites based on $LaCrO_3$ and $LaAlO_3$ and doped with 5% of a transition metal on the B site was found to have excellent activity for catalyzing the autothermal reforming of dodecane into a hydrogen-rich gas.
- The perovskites were shown to remain single phase in both reducing and oxidizing conditions, proving that the catalysis is occurring by redox chemistry on the B site and not on small metallic particles supported on an oxide matrix.
- The effect of 50 ppm of dibenzothiophene in dodecane was shown to be minimal.

Future Directions

- Optimize the composition of the catalysts in terms of activity for aromatics, aliphatics and other diesel components; cost; and sulfur tolerance.
- Determine the long-term stability.
- Work with a private sector organization on scaling up the process.

Introduction

Auxiliary power units (APUs) for heavy-duty vehicles could reduce emissions and conserve fuel where engines are kept running while drivers rest. An APU must have enough power to keep the cabin air-conditioned or heated in hot or cold climatic conditions, respectively, and may have to also supply electricity for refrigeration of loads. The amount of fuel needed will be significant, and drivers may resist having to refuel the APU with anything other than the diesel fuel used for the engine.

Converting diesel fuel into a hydrogen-rich gas that is suitable for solid oxide fuel cells is more challenging than converting gasoline because of the multi-cyclic aromatics and the aromatic sulfur compounds in diesel fuel. To break down these compounds, the operating temperature of the reformer needs to be raised, and the reforming catalyst needs to have a significant tolerance for sulfur. In making these statements, it is assumed that an autothermal reactor (ATR) [1] is used and that the diesel fuel is not desulfurized at the refinery.

When the operating temperature of the ATR exceeds about 800°C, catalyst stability becomes an issue. Noble metal catalysts such as rhodium, palladium or platinum on alumina or ceria not only lose some activity due to adsorption of hydrogen sulfide on the metal surface, but are further affected by evaporation and consolidation of the metal.

Approach

In earlier work at ANL to form noble metal ions, it was noticed that noble metals interact with supports containing oxide ion vacancies. It stands to reason, then, that the partial oxidation of hydrocarbon molecules might also be occurring on perovskite surfaces with B-site elements that can undergo redox reactions. Such catalysts would be expected to be more thermally stable than finely dispersed noble metals on alumina.

To be useful as an ATR catalyst, the perovskite must of course be chemically stable in oxidizing and reducing conditions. Lanthanum chromite and lanthanum aluminite meet that requirement. The first has some redox properties on the B site while the aluminite does not. However, doping with other transition metal elements on the B site can make the surface more active. In this paper, we report results of doping chromite and aluminite with ruthenium.

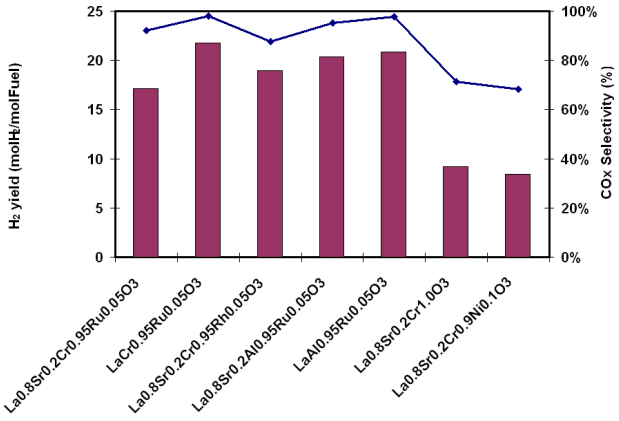

Figure 1. Hydrogen Yield (bar) and CO_x Selectivity (line) Obtained for Several Perovskite Catalysts during ATR Reforming

Results

Shown in Figure 1 are the hydrogen yields and COx selectivities obtained under the ATR reforming condition of $O_2/C = 0.5$ and $H_2O/C = 2$. The ruthenium-doped lanthanum chromite is clearly much more active than the undoped chromite or the nickel-doped chromite. To our surprise, strontium substitution on the A- site seems to diminish the activity somewhat. Similarly, the aluminite-based perovskites with ruthenium doping on the B site performed very well, proving that the activity is associated with the B site doping and not the B site host. We also found that ruthenium-doped chromite has similar catalytic activity, as measured by the hydrogen yield and COx selectivity, to that of rhodium-doped perovskite during the reforming of dodecane. This is rather enlightening considering the significant difference in raw material cost. Further study, of course, is necessary to verify whether comparable performance can be achieved under a wider range of catalytic conditions or types of fuels.

One may ask whether the ruthenium or the rhodium is in fact substituted for chromium or aluminum in the perovskite lattice or present as metals or oxides on the surface. Efforts are underway to answer this question using extended x-ray absorption fine structure (EXAFS).

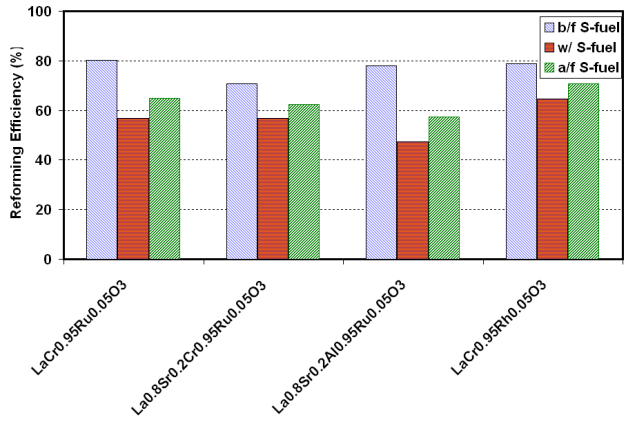

Figure 2. Total Reforming Efficiencies before, during, and after Exposure to DBT

Preliminary results indicate that the majority of the ruthenium and rhodium are anchored in the lattice.

One of the key challenges in diesel reforming is deactivation from sulfur poisoning. The current low-S diesel standard has sulfur content of 500 ppm with 350 ppm being typical. (In 2006, the sulfur limit drops to 15 ppm.) Unlike the case of gasoline, the organic sulfur compounds in diesel are from mainly polyaromatic molecules such as dibenzothiophene (DBT), methyl-dibenzothiophene, etc. These compounds are even harder to desulfurize and are expected to cause deactivation of reforming catalysts. Shown in Figure 2 are the total reforming efficiencies of the ATR reaction over four perovskite catalysts before, during, and after exposure to the fuel containing the organic sulfur for 150 minutes. (The maximum reforming efficiency ranges from 81% to 87% depending on the product distribution between H_2 and CO.) The deactivation occurs over all the catalyst samples tested, albeit at different degrees. However, a significant recovery was also observed after the sulfur-contaminated fuel was replaced by S-free fuel.

Conclusions

Ruthenium-doped perovskites have been shown to be effective catalysts for the autothermal reforming of dodecane, and to retain a significant level of activity in the presence of sulfur. Whether multicyclic aromatics that constitute a few percent of diesel fuel can be reformed as well remains to be investigated.

References

1. M. Krumpelt, T. R. Krause, J. D. Carter, S. Ahmed, Catalysis Today, 77 (2002), 3-16.